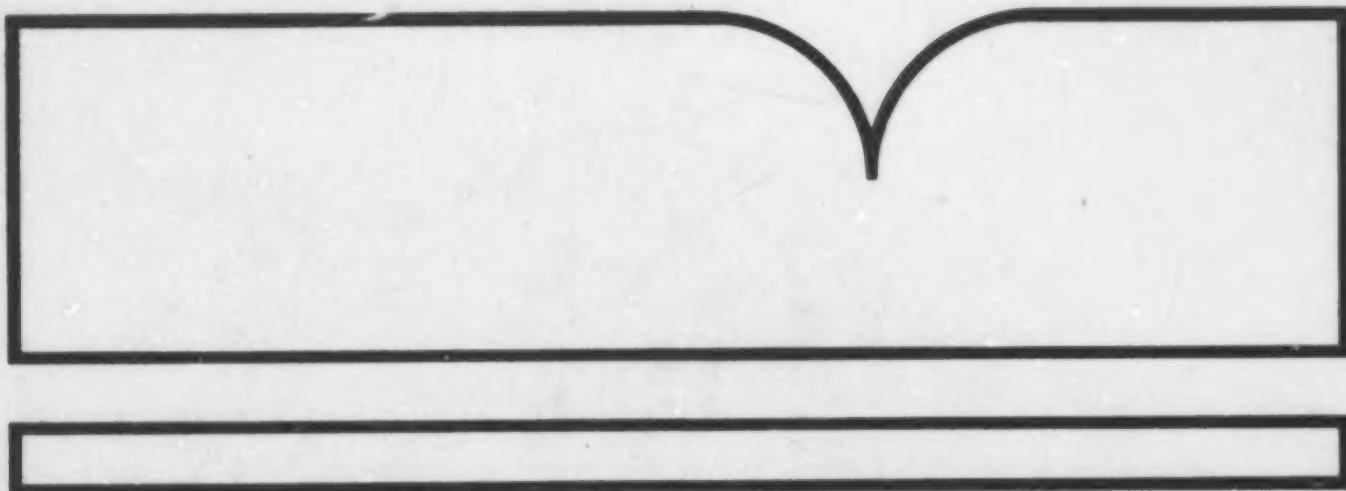


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Empirical Prediction of Organic Pollutant Sorption in Natural Sediments

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ABSTRACT

An empirical relationship between the octanol/water partition coefficients (K_{ow}) and sediment sorption coefficients (K_{oc}) was determined for nine chloro-s-triazine and dinitroaniline compounds. Results were compared with earlier work that reported an excellent correlation between K_{ow} and K_{oc} for polynuclear aromatic and chlorinated hydrocarbons. The more polar character of the present compounds, however, reduced the precision of estimating sorption from octanol/water partition coefficients. A fit of the combined data sets for a total of 19 compounds of widely varied properties (five orders of magnitude variation in solubility) yielded a relationship that should be useful for predicting simple partition coefficients (K_p) in a number of modeling and assessment applications. Reasonable estimates of K_p or K_{oc} can be obtained from a single determination of the octanol/water partition coefficient and knowledge of the organic carbon content of the sediment.

Additional Index Words: triazines, dinitroanilines, physical sorption, octanol/water partitioning.

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Recently, increased environmental interest has been directed toward obtaining quantitative information on pollutant sorption equilibria in soils and sediments. Information of this kind is necessary to permit a fundamental understanding of the various processes (biological availability and degradation, photochemistry, hydrolysis, and oxidation) affecting the fate of pollutants in natural systems. Increasing demands have also been felt for quantitative sorption data as inputs to various environmental models for evaluation or prediction of pollutant behavior in the environment. The importance of sediment/water partitioning has been amplified by emphasis on pollution control measures that are keyed to sediment transport.

The great diversity of compounds and sediment/soil combinations eliminates the possibility of measuring partition coefficients for all cases. At the same time,

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theoretical understanding of sorption processes in natural systems is not sufficiently developed to allow reliable estimates of partition coefficients from basic calculations. However, a useful approach for systematizing the estimation of partition coefficients empirically has been developed. Lambert (8) applied extrathermodynamic linear free energy relationships in relating sorption behavior to chemical structure. In these studies he successfully related the sorption equilibrium constant to parachor (a molecular volume parameter). Hance (4) modified the parachor relationship by adding a term to account for hydrogen bonding. These studies were some of the earliest attempts to systematize sorption responses based on chemical structure of the sorbate. Lambert (9) later attempted to systematize soil properties using a normalization parameter (Ω) expressing the active fraction of soil organic matter. Partition coefficients were linearly related to the organic matter contents of the sediments. Lambert also discussed sorption equilibria in terms of distributions in two-phase solvent systems and thin-layer chromatography measurements. These contributions, along with those of Goring (2) and Hamaker and Thompson (3), have evolved into a series of extrathermodynamically based relationships that correlate distribution coefficients in two-phase solvent systems with partitioning to the organic-C fraction of natural sediments.

Briggs (1) related organic matter/water partition coefficients for four Rothamsted soils and 30 compounds to the octanol/water partition coefficients. He also gave empirical equations relating octanol/water partitioning behavior to relative compound mobilities on soil thin-layer chromatographic plates. More recently, Karickhoff et al. (6) reported that sorption coefficients (K_{oc}) of polycyclic aromatic hydrocarbons were constant and independent of sediment type when expressed on a unit C basis. They defined K_{oc} by $K_{oc} = K_p/OC$, where K_p is the usual partition coefficient expressing the ratio of sorbate concentration on the sediment to that in the solution, and OC is the decimal fraction organic-C in the sediment. Karickhoff et al. also related K_{oc} to the octanol/water partition coefficients of the same compounds. A good linear relationship was obtained even though the solubilities of compounds tested ranged over several orders of magnitude. Thus, for a series of hydrophobic materials, it was possible to estimate sediment/water partition coefficients for a variety of natural sediments from a single liquid/liquid partitioning experiment. The utility of this approach lies in the fact that the octanol/water partition coefficient is more easily attainable than sorption coefficients for particular sediments. Kenaga and Goring (7) have summarized this and a number of similar equations. Leo (10) and Leo et al. (11) have shown that K_{ow} for many compounds are amenable to calculation from a well-developed listing of substituent constants. These facts, along with recent use of octanol/water partition coefficient in assessing environmental behavior of new compounds, have combined to make K_{ow} values increasingly more available for a wide range of compounds. Consequently, empirical relationships similar to those developed by Karickhoff et al. show promise as predictive tools for estimating sorption in natural systems.

The purpose of this work was to test and expand this kind of relationship to compounds having more diverse substituent groups. Several members from the chloro-s-triazine and dinitroaniline groups were selected for study.

MATERIALS AND METHODS¹

Sediment Preparation

The sediment was isolated from bottom samples of a small, northern Georgia pond (Hickory Hill). The coarse silt fraction (20–50 μ m) was isolated by sedimentation and washed (resuspended and sedimented) five times to remove occluded fines. Galbraith Laboratories Inc., Knoxville, Tenn., determined the organic-C as total-C (Leco dry combustion) minus inorganic carbonates (gas purge of acidified suspensions).

Sorption Isotherms

Details of the sorption isotherm procedures varied somewhat depending on properties of the individual compounds under examination. These compounds included a triazine group and a dinitroaniline group. The triazine group consisted of atrazine [2-chloro-4-(1-cyano-1-methylethylamino)-6-ethylamino-s-triazine], cyanazine [2-chloro-4-(1-cyano-1-methylethylamino)-6-ethylamino-s-triazine], ipazine [2-chloro-4-(diethylamino)-6-(isopropylamino)-s-triazine], propazine [2-chloro-4,6-bis-isopropylamino-s-triazine], and simazine [2-chloro-4,6-bis-ethylamino-s-triazine]. The dinitroaniline group was made up of trifluralin (2,6-dinitro-*N,N*,di-*n*-propyl- α,α,α -trifluoro-*p*-toluidine) and two of its degradation products. Products I and II were 2,6-dinitro-*N*-*n*-propyl- α,α,α -trifluoro-*p*-toluidine and 2,6-dinitro- α,α,α -trifluoro-*p*-toluidine, respectively.

Construction of each isotherm consisted of independently measuring equilibrium sorbate concentrations in both the water and sediment phases at six different points along the isotherm. Each isotherm was replicated from two to four times depending on scatter in the data. Test conditions were established by adding predetermined volumes of the sorbate solutions to erlenmeyer flasks in hexane (dinitroanilines) or methanol (triazines). The solvents were evaporated under an air stream leaving a thin film of sorbate crystals on the walls of the flask. One-gram increments of the air-dried coarse silt and 50 ml of distilled water were added to the resulting flasks. In all cases, the added maximum solution concentration after equilibration with the sorbent did not exceed approximately 50% of the water solubility. Solution concentrations varied from a few parts per billion for the most insoluble compound (trifluralin) to a few parts per million for the triazines.

Flasks containing the water/sediment mixtures were equilibrated using a gentle swirling action in an orbital shaker at $25(\pm 1)^{\circ}\text{C}$ until no further concentration changes could be detected. Equilibration times ranged from a minimum of 24 hours (triazines) to a maximum of 72 hours (trifluralin), as required. The reaction vessels were sealed with stoppers wrapped in aluminum foil to minimize sorption.

After equilibration, the phases were separated by centrifugation at 20,000 rpm (Sorvall RC2-B with SS-34 rotor) for 60 min in 50-ml stainless steel, air-tight tubes. The tube caps were wrapped in aluminum foil to eliminate sorption by the rubber cap seals. Temperature in the centrifuge was $25(\pm 3)^{\circ}\text{C}$. Aliquots of the solution phase were transferred to separatory funnels and extracted with either hexane or methylene chloride depending on the compound in question. Multiple extractions were used as needed for the more soluble compounds that gave <90% yield after a single extraction. The methylene chloride extracts were evaporated to dryness under an air stream, and reconstituted with hexane or methanol for analysis.

Sediment phase samples were collected on a filter disc in porcelain Buchner funnels to remove excess moisture, and the filter containing the sediment was transferred to Soxhlet extractors. Extraction times necessary for good recovery ranged from a minimum of 4 hours for the triazines to 24 hours for trifluralin. The extraction solvents were

¹Mention of commercial products or trade names does not constitute endorsement or recommendation for use by the United States Environmental Protection Agency.

methylene chloride for the triazines and hexane for the dinitroanilines. Methylene chloride was eliminated as above for compatibility with the gas chromatograph.

Final analyses of all samples were performed on a Tracor model MT-222 gas chromatograph equipped with ^{63}Ni electron capture and model 700 Hall electrolytic conductivity detectors. The 1.8 by 0.02 m i.d. column was packed with 10% DC 200 on Gas Chrom Q. Triazines were determined on a Hall detector operated in the N mode and the dinitroanilines were analyzed by electron capture. Output signals were processed by a Varian CDS 111 integrator system.

Octanol/Water Partitioning

Octanol/water partition coefficients were determined using reagent grade octanol that had been extracted once with 0.1N NaOH and twice with distilled water, and distilled twice. Stock solutions of the test compounds were prepared in octanol, and 2 ml of each was equilibrated with 40 ml of distilled water in closed stainless steel centrifuge tubes. Resulting samples were equilibrated for 15 min on a wrist-action shaker and phases were separated by centrifugation at 15,000 rpm (Sorvall SS-34 rotor) for 15 min. One-ml aliquots of the octanol phases were diluted 100- to 10,000-fold in appropriate solvents and injected directly. Samples from the water phase were extracted with either hexane, benzene, or methanol. Where necessary for adequate recovery, multiple extractions were used.

Additional determinations were performed as a check using direct UV spectroscopic analysis of the water phase.

RESULTS AND DISCUSSION

The relationship established by Karickhoff and co-workers (6) between the octanol/water partition coefficients for a group of hydrophobic organic compounds and the respective sorption coefficients in natural stream sediment systems was expressed in the following forms:

$$K_{oc} = 0.63 K_{ow}, \text{ and} \quad [1]$$

$$\log K_{oc} = 1.00 \log K_{ow} - 0.21, \quad [2]$$

where

$$K_{oc} = K_p/OC, \quad [3]$$

in which K_p is the sediment water partition coefficient expressed as the ratio of sorbate concentration in the sorbed (sediment) phase ($\mu\text{g/g}$) over that in the equilibrium solution ($\mu\text{g/ml}$), and OC is the fraction of organic-C in the test sediment.

Viewing sorption in this way embodies two general assumptions. Representation of the sorption isotherm by a simple partition coefficient (K_p) requires that the isotherm be linear. In defining K_{oc} , one must assume that mineral components in the sediment are not significantly active in the sorption process. Karickhoff et al. (6), using Hickory Hill sediments from the same source as in the present work, established that both these criteria were met in their series of experimental systems. They also fractionated the whole sediments into fine particle size separates and determined K_p for pyrene and methoxychlor on each fraction. While K_p for the silts and clay varied widely between fractions, the variation was largely normalized by organic-C content, yielding nearly constant K_{oc} . This suggests that the organic sorbents present in the various fines fractions behaved similarly. Humic materials associated with the sand

Table 1—Hickory Hill silt sorption isotherm partition coefficients (K_p), organic-C weighted sorption coefficients (K_{oc}), and octanol/water partition coefficients (K_{ow}) for selected compounds.

Compound	K_p	K_{oc}	$\log K_{oc}$	K_{ow}	$\log K_{ow}$
Atrazine	7.07	216	2.33	513 ± 77	2.71
Cyanazine	5.98	183	2.26	176 ± 30	2.24
Ipazine	26.6	813	2.91	$8.74(\pm 2.96) \times 10^3$	3.94
Propazine	11.9	363	2.56	873 ± 136	2.94
Simazine	7.04	216	2.33	146 ± 56	2.16
Trietazine	17.9	547	2.74	$2.26(\pm 0.41) \times 10^3$	3.35
Trifluralin	999	30,550	4.49	$2.08(\pm 0.84) \times 10^3$	5.28
Product I†	132	4,040	3.61	$4.46(\pm 0.45) \times 10^3$	3.65
Product II‡	11.9	364	2.56	195 ± 4.9	2.29

† 2,6-dinitro-N-n-propyl- α,α,α -trifluoro-p-toluidine.

‡ 2,6-dinitro- α,α,α -trifluoro-p-toluidine.

fraction were less efficient, and because of their low concentrations made a small contribution to sorption of the sediment as a whole. Other sediments investigated behaved similarly.

More recently, Hassett et al. (5) tested the K_{oc} relationship on a set of 13 soils and sediments using a collection of 14 test compounds selected from around the nation. Organic-C components in soils and sediments behaved indistinguishably relative to sorption. The K_{oc} vs. K_{ow} relationship established was in good agreement with that of Karickhoff et al. (Eq. [2]). Hassett and co-workers' regression equation on the combined data sets took the following form:

$$\log K_{oc} = \log K_{ow} - 0.317. \quad [4]$$

In lieu of this background, a full series of tests were not repeated here. The same Hickory Hill coarse silt fraction was selected for the tests. As in the previous study, all compounds investigated here gave linear isotherms over the concentration ranges investigated. Regression lines on the data sets gave r^2 values between 0.99 and 0.76 with a mean of 0.94.

The relative importance of organic and mineral sorbents for triazine sorption is apparent from Walker and Crawford's work (12). Their data shows a linear correlation between K_p and the sorbent C content for atrazine and propazine on 25 soils varying from very low to as much as 25% organic-C. It should be noted, however, that both the isotherm linearity and organic-C correlation can fail in systems where the test compound is protonated. This is probably the case for several of the other triazines, some of which were included in Walker and Crawford's study. Generally, a good correlation between K_{oc} and K_{ow} is reasonable in systems having nonspecific physical sorption of neutral molecules as the predominant process. Conditions favoring sorbate dissociation, protonation, or chemical interaction with the surface would be expected to introduce nonlinearity and/or negate the assumption that organic materials are the primary sorbent. As an additional constraint, sorbate concentrations in both the sorbed and solution phases must be sufficiently dilute to avoid precipitation or surface loading sufficient to significantly alter the character of the surface.

The foregoing restrictions do not greatly limit the use of empirical K_{oc} vs. K_{ow} relationships for estimating sorption coefficients for the majority of natural sys-

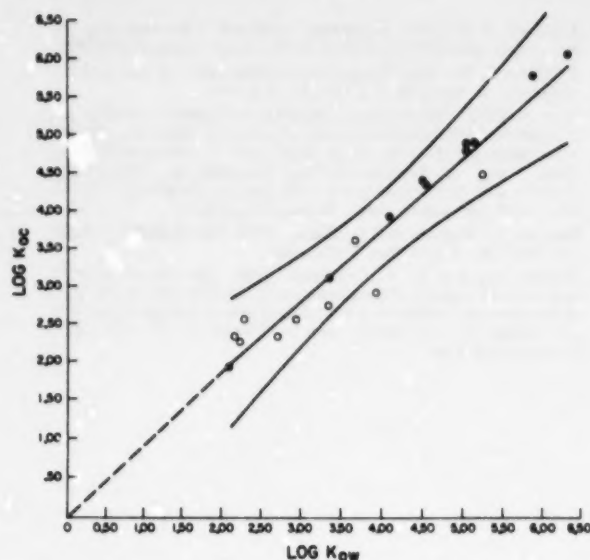


Fig. 1—Relationship between $\log K_{oc}$ and $\log K_{ow}$ for Hickory Hill coarse silt. Superimposed data (●) from Karickhoff, Brown, and Scott, 1979.

tems. Pollutant concentrations commonly encountered in stream systems are nearly always low enough to be within the linear range of the sorption isotherm. Also, many organic pollutants, having sorption as a key determinant of environmental fate, are highly insoluble. Examples include chlorinated hydrocarbons, polycyclic aromatics, and polychlorinated biphenyls. These materials are strongly hydrophobic and interact with the sorbent as neutral molecules.

Successful normalization of sorption coefficients for the organic-C contents of the respective sediments reduces the number of sediments that must be studied. Additionally, after demonstrating a K_{oc} vs. K_{ow} correlation for a few members of a given family of compounds, one might reasonably expect to obtain good estimates of K_p for other members of the family based on K_{ow} alone. Generalizing one step further, one could expect a single empirical K_{oc} vs. K_{ow} relationship to extend to several families of compounds, thus reducing the number of relationships required to cover compounds of interest. Ideally, only one equation would suffice for all compounds amenable to this treatment. This would allow estimation of K_p for any sediment from a single K_{ow} determination. Introducing a greater diversity of chemicals would be expected to reduce the precision of individual estimates but should better define the confidence limits for a broader range of materials.

Experimental partition coefficients determined for the nine test compounds in the sediment and octanol systems are given in Table 1. Figure 1 shows the logarithms of partition coefficients from Table 1 superimposed on similar data reported by Karickhoff et al. (6) for a series of polycyclic aromatic hydrocarbons (PAHs) and chlorinated hydrocarbons. Linear regression of the combined data sets resulted in the following empirical equation:

$$\log K_{oc} = 0.937 \log K_{ow} - 0.006 \quad r^2 = 0.95. \quad [5]$$

Inclusion of the triazines and nitroanilines with the less polar, more hydrophobic compounds resulted in a significant increase in uncertainty ($r^2 = 1.00$ and 0.95 , respectively) in Eq. [4] relative to Eq. [2], developed by Karickhoff and coworkers. This behavior is to be expected in that the present group of compounds are influenced by their functional groups. Specific functional group interactions with surface sites are not explicitly accounted for in the K_{oc} treatment. It is important to note that, although interactions of this type resulted in greater uncertainty, the variations were largely random. Inclusion of the polar materials with the compounds reported by Karickhoff and coworkers changed the coefficients in Eq. [2] only slightly. Actual errors in predicting K_p from K_{oc} or K_{ow} data arising from specific surface interactions may be attenuated in natural sorbent systems. The often-noted correlations between organic-C content and cation exchange capacity or surface area would tend to lessen possible errors.

The practical utility of Eq. [5], or others like it, is maximized when the range of compounds it can be used to treat is very broad. Better precision could be obtained by fitting separate equations to less diverse groups of compounds, but doing so would reduce the applicable range. Ultimately, the choice lies in establishing the precision required for a given use. Predicted $\log K_{oc}$ values from Eq. [4] at the 90% level are ± 0.254 at the high end of the curve, ± 0.209 at the low end, and ± 0.113 at the midpoint. Taking the worst case and using atrazine as an example, the predicted K_{oc} would have a range of 195–617. For a sediment of 3.27% organic-C, the range in K_p would be 6.38–20.2, or roughly a factor of three. Using figures for the mid-range of the curve, the best case example would yield a K_p range of 8.60–14.9, less than a factor of two.

SUMMARY

Sorption isotherms for nine compounds from the chloro-s-triazine and dinitroaniline groups were linear. Sorption coefficients expressed on a unit C basis were empirically related to the corresponding octanol/water partition coefficients. Estimates of K_p based on the empirical equation were within a factor of two or three of the measured values. Predictions of this quality would be adequate for many environmental modeling applications. Equations given provide a basis for predicting sorption coefficients for natural sediments from a determination of the octanol/water partition coefficient and the organic-C contents of the sediments.

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